SEPARATION OF CAROTENE FROM CRUDE PALM OIL BY MEMBRANES

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Abstract

Malaysia is the world's largest producer and exporter of palm oil. The production figure in 1995 was 7.6 million tonnes and it is anticipated that by the year 2000, the country's production can easily attain 8.8 million tonnes. Palm oil and its products which are exported are in refined, bleached and deodorized forms. This means that the present refining process in Malaysia causes the destruction of most of the minor components (carotenoids, sterol, tocopherol and tocotrienols) in the crude oil.

Membrane applications and research in the edible oil industry are well documented in recent years. Separation of minor components from crude palm by membranes is a new technique. At UTM, research has been initiated to study the possibilities of using membranes to separate carotene from crude palm oil. Preliminary laboratory studies have been conducted by using carotene rich palm olein as the raw sample. A static test cell with effective tested diameter of 22mm and feed volume of 30ml was used. Two types of new class of solvent stable membranes which has been developed with cutoffs in the nanofiltration and UF ranges have been employed. Solvent permeation rates, and separation performances of the membranes were determined by using commercial extraction solvents such as hexane and methanol. Optimum operating parameters and conditions which effects the separation performance such as pressure and flux rates have been studied. Initial laboratory investigations have shown encouraging results with 50% separation of the carotene.

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Introduction

Malaysia is the world's largest producer and exporter of palm oil. The production figure in 1995 was 7.6 million tonnes and 60% of this was exported1. Palm oil and its products which are exported are in refined, bleached and deodorized forms. This means that the present refining process in Malaysia causes the destruction of most of the carotenes present in the crude oil. As a result the final product is light golden colour and devoid of carotenes. It also means that palm oil refining has allowed 3170-4398 tonnes of carotene's to be destroyed in 1995. Of all the natural fats and oils, palm oil has the most abundant composition of carotenoids (about 600 parts per million). Global production of palm oil is expected to increase to about 20 million tons by the year 2005. Malaysia will contribute about half of this total.

The carotenoid content of crude palm oils (CPO) from Malaysia and Zaire varies between 500 and 700 ppm (Goh *et al.*, 1985); larger amounts (800 - 1600 ppm) from Dura species have been reported from Nigerian sources. A typical analysis of the composition of the carotenoids shows that alpha- and beta-carotenes are the major components, and the rest are gamma-carotene, lycopene and xanthopylls. The presence of high content of beta-carotene causes the palm oil to have deep orange colour. In fact, crude palm oil is the richest natural plant source of carotenes in terms of retinol (pro vitamin A) equivalents. It has 15 times more retinol equivalents than carrots and 300 times more than tomatoes.

Beta-carotene is the most common precursor of vitamin A which functions as a promoter of good night vision, healthy mucous membrane and skin, and the growth of the bone and its reproduction. Enzyme converts the beta-carotene as is required. Epidemiological studies in the 1980's strongly associated beta-carotene with the prevention of certain types of cancers, such as oral, pharyngeal, lung, and stomach cancer (Choo *et al.*, 1996). In fact, the National Institutes of Health has identified beta-carotene as one of the top-ten cancer preventive agents. What is more interesting is the recent report on tenfold more potent as an anti-cancer agent than beta-carotene. In addition, a recent study has also indicated that beta-carotene possesses an anti-atherosclerotic effect because it is able to lower plaque levels in arteries.

Most of the available supply of beta-carotene is 90% from chemically synthesized beta-carotene, with natural beta carotene accounting for 10% of the market share (Yacob, 1992). The demand for natural beta carotene is growing at higher pace compared to the synthetic equivalent due to its perceived safety. It is envisaged that in the long run the market for natural beta carotene could easily grab 25% of the overall market by the year 2000. The anticipated annual growth of the market for natural beta carotenes is greater than 20%.

Many attempts have been made to recover carotene from crude palm oil, and most of these depend either on chemically transforming the triglycerides, e.g. saponification or transesterification. The only commercially viable process, so far, is transesterification followed by phase separation. It involves transesterification of triglycerides with

methanol to yield methyl ester, followed by phase separation, resulting in a carotene-rich layer and a decoloured methyl ester layer. The carotene-rich layer is further concentrated by molecular distillation and chromatographic methods. Unfortunately, the disadvantage of this process is that edible oil i.e. triglyceride is not obtained as the remainder palm oil and is chemically converted (Baharin, 1993).

Membrane Technology in Oil & Fats Industry.
Application of membrane separation processes in the oils and fats industry have recently attracted a great deal of attention. A considerable amount of exploratory work has been done in the areas of hexane recovery from oil miscella, vapor recovery, condensate return, degumming, refining and bleaching, hydrogenation catalyst recovery, waste-water treatment, and others (Krishna Kumar and Bhowmick, 1996). In allied industries, membrane separation has found good application in recovery and purification protein. Membrane processes have been investigated primarily for thier energy efficiency and selectivity. Deacidification of oils and fats is most widely done by alkali refining. Physical refining has also been suggested as a possible replacement for alkali refining. However,, the application of membrane technology in edible oil industry has not developed as much as the other areas of the food processing, mainly due to the non-availlability of stable membranes. Recently, however, newly-available, non-aqueous (hexane resistant) membranes created opportunities that can be applied to edible oil processing.

Because of the significance and potential of the method, most of the information has been kept confidential and only limited amount of work has been published in the patent literature. Membrane processing of crude vegetable oils was studied by Koseoglu et al., 1990. The study was on separation of vegetable oils from commercial extraction solvents using various types of Reverse Osmosis (RO) and Ultrafiltration (UF) membranes. Solvent permeation rates and separation performance of various RO and UF membranes were determined by using ethanol, isopropyl alcohol and hexane as the solvents. Separation of fatty acids from triacyglycerol by membrane separation technique has been studied by Krishma Kumar and Bhowmick (1996). Mixtures of triacylgycerols and fatty acids were extracted with alcohol, and the alcohol extracts were treated for recovery of oil by membrane separation technique.

Preliminary Experimental Study

Oil-Solvent Mixtures.
Oil-solvent mixtures, were prepared by mixing commercially available carotene rich cooking oil (Carotino) with commercial hexane in different ratios. Hexane was permeated through each membrane to provide a reference permeation rate.

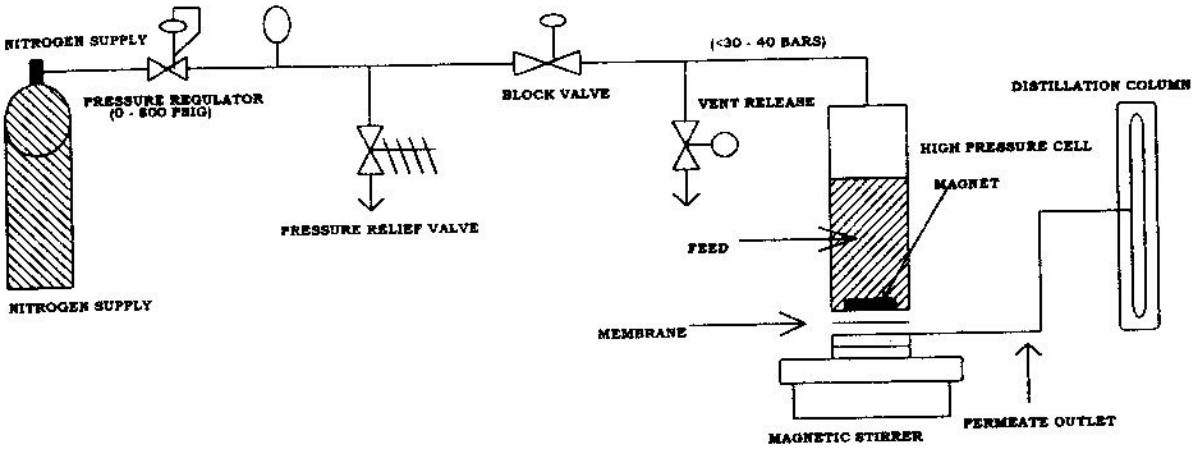

FIGURE 1. EXPERIMENTAL SET-UP OF TEST CELL

Membrane Separation Trials.
Membranes and the test cell (Figure 1) were procured from leading membrane manufactures. Membrane employed had an MWCO (molecular weight cut-off) between 400 - 700D and the pressure requirements were not high with maximum operating pressure 40 bar. Two types of membranes, namely A and B with MWCO 700 and 400 respectively have been used. The membranes are chemically stable particularly with hexane and separates low MW organics in 100% organic solvents. Solvents used were of analytical reagent-grade (A.C.S. analar grade). Different test samples as feed for various experiments were made by and a constant pressure of 30 bar was employed at an ambient temperature 27°C.

Carotene Analysis.
Determination of carotene content was carried out by following closely standard methods of PORIM p2.6 (1995). Spectrophotometric measurement at 446 nm of the absorbance was used with 2,2,4-trimethylpentane (iso-octane) reagent.

Results and Discussion

The general characteristics of membranes used are given in Table 1. Both membranes have a temperature tolerance of 40°C which is an ideal condition to separate the carotene at ambient temperature. Results indicated that, apart from having an excellent solvent stability, the membranes can withstand high pressures, with maximum pressure of 40 bar. Fluxes and linear flow velocity tested for various commercially available solvents and membranes are given in Table 2. For the A membrane, the flux rates indicated that, it has higher value compared to A membrane, presumably because of its high MWCO. However, the two membranes maintained linear flow velocity values at 17m/sec. This information is useful for predicting the behavior of the membrane material for the intended application.

TABLE 1
GENERAL CHARACTERISTIC OF THE MEMBRANES

	A	B
Molecular weight cut-off	400D	700D
pH tolerance	2 - 10	2 - 10
Temperature tolerance	40°C	40°C
Solvent stability	excellent	excellent
Maximum pressure	35 bar	40 bar

TABLE 2
MEMBRANE PERFORMANCE

	A	B
Flux for solvents:		
Hexane	30 l/m^2.h	45 l/m^2.h
Methanol	40 l/m^2.h	52 l/m^2.h
Water:	0 l/m^2.h	0 l/m^2.h
Linear flow velocity	17 m/sec	17 m/sec

Table 3 and 4 shows the carotene analysis of concentrate and the permeate or product. The values justifies that they is some separation of carotene. In other words, membrane can be used to separate minor components, particularly the carotenes in this study.

TABLE 3
CAROTENE ANALYSIS OF THE CONCENTRATE IN THE TEST CELL

TRIAL	SAMPLE	MEMBRANE	RATIO	CAROTENE, ppm
1.	Carotino:Hexane	A	1:9	529
	Carotino:Hexane	B	1:9	570
2.	Carotino:Hexane	B	1:9	570
3.	Carotino:Hexane	B	1:9	554

TABLE 4
CAROTENE ANALYSIS OF THE PERMEATE

TRIAL	SAMPLE	MEMBRANE	RATIO	CAROTENE, ppm
1.	Carotino:Hexane	A	1:9	600
	Carotino:Hexane	B	1:9	630
2.	Carotino:Hexane	B	1:9	670
3.	Carotino:Hexane	B	1:9	572

Flux value and time were determined and it is shown in Figure 2. The maximum flux for membrane A is 7.1 $lm^{-2}h^{-1}$ and for membrane B is 6.65 $lm^{-2}h^{-1}$. The figure shows the flux behavior as a function of time. Results indicated that, the membrane performance (or the system performance) may change with time. In another word, the flux through the membranes decrease over time. Flux decline can be caused by several factors, such as concentration polarization, adsorption, gel-layer formation and plugging of the pores. All these factors induce additional resistance on the feed side to the transport across the membrane.

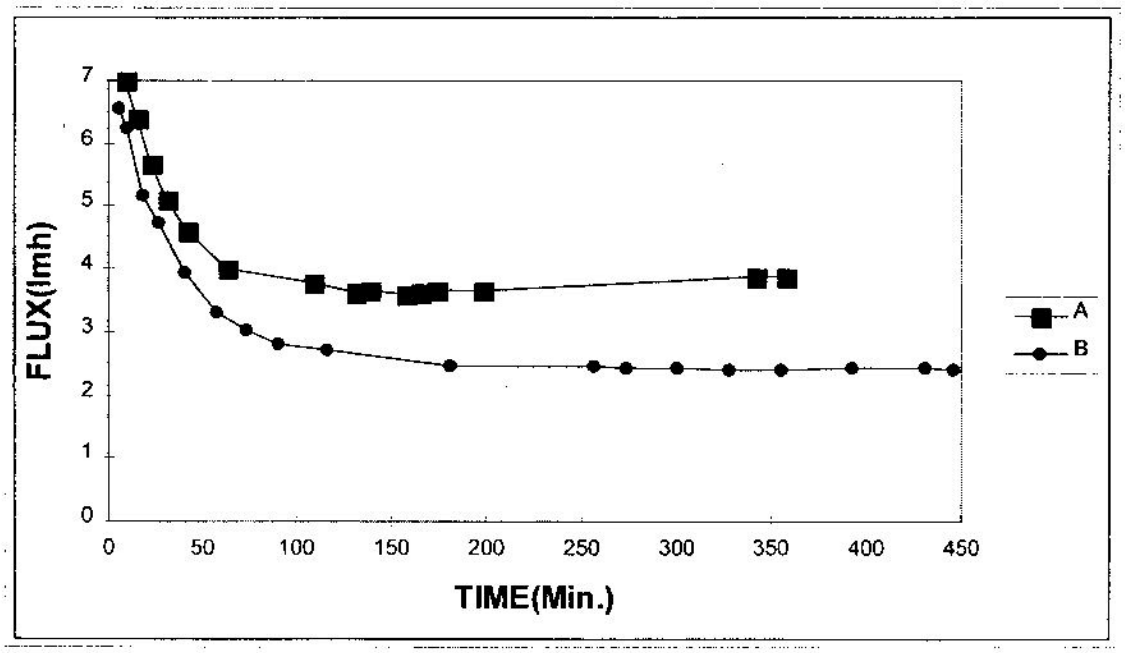

FIGURE 2. FLUX BEHAVIOUR AS A FUNCTION OF TIME FOR CAROTINO:HEXANE;1:9

Conclusion

Based on experimental results, it is concluded that membrane can be used for the separation of minor components, particularly carotenes. Further studies are to be carried using CPO and other type of solvents, such as IPA (Iso-Propyl Alcohol), Ethanol, etc. It is proposed that a pilot plant scale of this process to be constructed. This would make it possible for optimization studies be conducted for further scale-up to industrial scale. Besides that, the carotene extracted from the pilot plant studies can still be sold as a finished product.

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